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Chemical Characteristics and Oxidative Potential of Particulate Matter Emissions from Gasoline, Diesel, and Biodiesel Cars

KA LAM CHEUNG,[†] ANDREA POLIDORI,[†] LEONIDAS NTZIACHRISTOS,[‡] THEODOROS TZAMKIOZIS,[‡] ZISSIS SAMARAS,[‡] FLEMMING R. CASSEE,[§] MIRIAM GERLOFS,[§] AND CONSTANTINOS SIOUTAS*,[†]

Department of Civil and Environmental Engineering, University of Southern California, 3620 South Vermont Avenue, Los Angeles, California 90089, Laboratory of Applied Thermodynamics, Aristotle University, Thessaloniki 54124, Greece, and Center of Environmental Health Research, National Institute for Public Health and the Environment (RIVM), P.O. Box 1, NL-3720 BA Bilthoven, The Netherlands

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Three light-duty vehicles in five different configurations [a Honda Accord operating with diesel with a closed-coupled oxidation catalyst and an underfloor catalyst replaced in some tests with a diesel particle filter (DPF), a Toyota Corolla operating with gasoline, and a VW Golf alternatively operating with petrodiesel or biodiesel] were tested in a dynamometer facility to develop an improved understanding of the factors affecting the toxicity of particulate exhaust emissions. The vehicles were tested using a variety of real-world driving cycles, more than the certification test (New European Driving Cycle). Particle samples were collected and analyzed for elemental and organic carbon (EC and OC, respectively), water soluble and water insoluble organic carbon (WSOC and WISOC, respectively), and inorganic ions, and the emission rates (mg/km) for each vehicle/configuration were determined. A dithiothreitol (DTT) assay was used to assess the oxidative potential of the particulate matter (PM) samples. The DPF-equipped diesel and gasoline vehicles were characterized by the lowest overall PM mass emissions, while the diesel and biodiesel cars produced the most potent exhaust in terms of oxidative activity. When the DPF was fitted on the Honda Accord diesel vehicle, the mass emission rates and distance-based oxidative potential were both decreased by 98%, compared to the original configuration. Correlation analysis showed that the DTT consumption rate was highly associated with WSOC, WISOC, and OC ($R = 0.98$, 0.93, and 0.94, respectively), consistent with previous findings.

1. Introduction

Exposure to particulate matter (PM) has been associated with numerous adverse health effects (*1*, *2*) and several studies have specifically linked vehicle-related PM exposure to premature deaths (*3*, *4*). Combustion processes represent the main source of PM in urban metropolitan areas (*5*); these include primarily motor vehicles emissions (*6*) but also wood burning, food cooking, and other combustion activities (*7*). The state of California classified diesel PM as a toxic air contaminant in 1998 due to its carcinogenic properties, its potential to cause respiratory and cardiovascular health problems (*8*, *9*), and its ability to induce allergic reactions (*10*). Diesel PM is also associated with several other environmental problems, including visibility degradation and global warming.

Despite recent advancements in toxicological research in the air pollution field, the relationship between particle properties (e.g., size, surface area, and composition) and specific health end points is still not completely understood. A few mechanisms have been proposed to explain health impacts of PM, including production of reactive oxygen species (ROS) and consequent generation of oxidative stress (*11*). Substantial evidence corroborates the ability of ultrafine and fine particles ($PM_{0.1}$ and $PM_{2.5}$, respectively) to induce oxidative stress in cells through the production of ROS that may lead to adverse health outcomes (*12*, *13*). Both chemical and biological assays are available to quantitatively characterize the production of ROS (see the Methods section for further details).

A better understanding of how the toxicity of vehicular PM varies with its chemical characteristics is vital in designing more effective emission control technologies. The primary objective of this study is to provide insights on the factors affecting the toxicological potential of exhaust PM emissions from different light-duty vehicles. Light-duty diesel vehicles are widespread in Europe and have been introduced in the U.S. with the 2009 model year, due to their higher fuel efficiency compared to gasoline vehicles. Compared to the heavy-duty vehicles, light-duty ones differ with respect to combustion tuning and aftertreatment (*14*). It is, therefore, important to assess the potential implications of the introduction of diesel cars regarding composition and toxicity of the emitted PM. This was accomplished by testing several diesel and gasoline cars operating with and without aftertreatment devices. Moreover, a biodiesel fuel vehicle was tested to assess the environmental and toxicological impacts of this new type of diesel fuel.

2. Methods

2.1. Testing Facility. Experiments were conducted at the light-duty dynamometer facility of the Laboratory of Applied Thermodynamics at Aristotle University in Thessaloniki, Greece. The exhaust of the tested vehicles was transferred by means of an insulated 6 m long corrugated stainless steel tube to a constant volume sampling (CVS) dilution tunnel, where an orifice forced rapid mixing with the dilution air. A positive displacement pump was used to control the nominal flow rate of the diluted exhaust gas at 600 Nm^3/h through the tunnel. Further details about the dynamometer facility are described in our previous publications (*15*, *16*).

A summary of the tested vehicles is shown Table S1 (see the Supporting Information). The newest vehicle was a 2.2 L "Euro 4" compliant diesel passenger car (Honda Accord 2.2 i-CTDi) equipped with exhaust gas recirculation and a three-stage oxidation aftertreatment system. This consisted of a closed-coupled oxidation catalyst (precatalyst) and a main underfloor catalyst formed of two monoliths in series. The same vehicle was also tested in an alternative configuration, with its main oxidation catalyst replaced by a diesel

* Corresponding author e-mail: sioutas@usc.edu.
[†] University of Southern California.
[‡] Aristotle University.
[§] National Institute for Public Health and the Environment.

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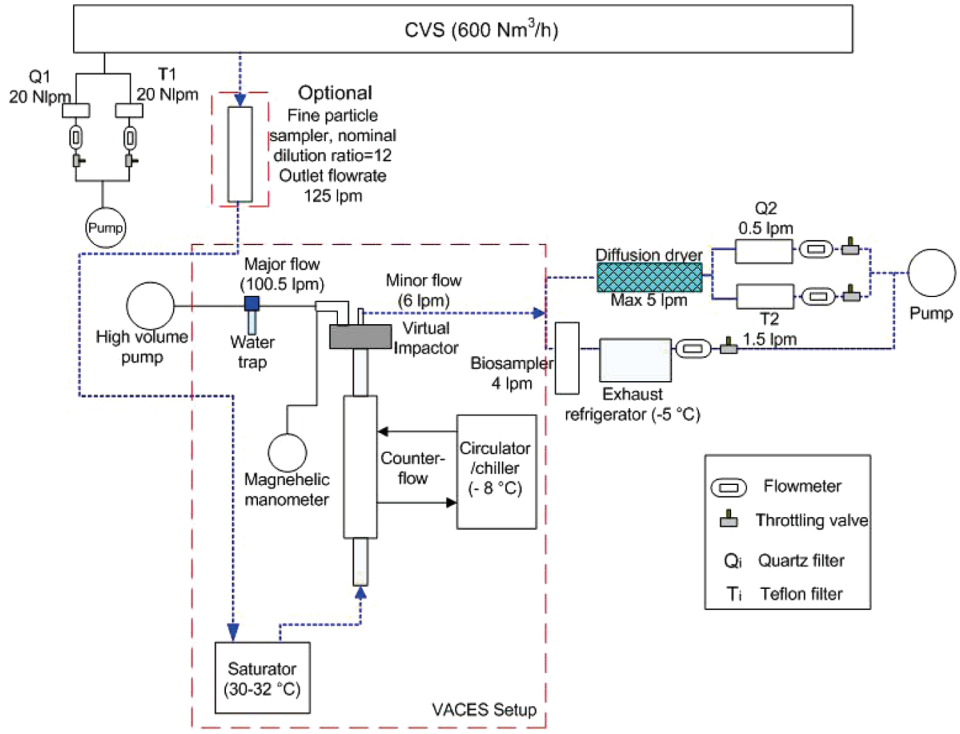

FIGURE 1. Schematic of the sampling system used for particulate matter collection.

particle filter (DPF). The DPF was a Pt-coated SiC filter of octagonal channel cross-section with 300 cells/in.^{2}. In this configuration, the vehicle complies with the "Euro 5" (2010) emission standards with regard to its PM emission levels. Hence, it is designated as "Euro 4+" in Table S1 in the Supporting Information. This car operated on low sulfur (<10 ppm) diesel fuel and lube oil with a sulfur content of 8900 ppm wt in both configurations.

The second car was a gasoline Toyota Corolla 1.8 L equipped with a three-way catalytic converter and twin lambda sensors, meeting the "Euro 3" emission standard. Unleaded gasoline with a research octane number (RON) of 95 and fully synthetic lube oil were used. The vehicle was equipped with the typical aftertreatment technology used for gasoline cars in Europe and in the U.S.

The third vehicle was an older diesel passenger car (Volkswagen Golf 1.9 L), originally equipped with an oxidation catalyst ("Euro 2" compliant). The catalyst was removed in the "baseline" configuration to represent diesel emissions with no exhaust aftertreatment. Diesel fuel with a nominal sulfur content of 50 ppm wt was used. This is designated as "Euro 1" in Table S1 in the Supporting Information. The same car was also run on 100% (neat) soy biodiesel with its oxidation catalyst in place. Biodiesel is technical jargon for fatty acid methyl ester (FAME) fuels, derived by the esterification of vegetable oils. The intent of these tests was to assess how fuels promoted the improvement of climate change impacts from transportation performance in terms of conventional pollutant emissions. This particular biodiesel is characterized by a near-zero sulfur content (2 ppm wt), a mass-based ester content of 96.6%, and a gross heating value of 38 MJ/kg. More information on the particular fuel is given by Fontaras et al. (*16*). Semisynthetic lube oil was used, as in both configurations.

Each vehicle was driven on a chassis dynamometer over driving cycles designed to cover a range of driving conditions. The measurement protocol, which was the same for every vehicle, consisted of a cold-start New European Driving Cycle (NEDC) and the series of the so-called Artemis cycles. NEDC consists of four repeated urban subcycles with a max speed of 50 km/h and an extra-urban driving subcycle (EUDC) reaching a top speed of 120 km/h The Artemis cycles were developed in the Artemis project (*17*) and were designed to simulate typical driving conditions in Europe. They consist of more frequent speed variation and stronger acceleration compared to the NEDC and represent real-world driving conditions. All vehicles were also tested at a steady speed of 90 km/h to obtain particle size distribution data.

Each vehicle and the sampling system were conditioned by running three EUDC tests before the actual measurements, in accordance to the PMP protocol (*18*). After conditioning, the vehicle was left to soak for at least 8 h in order to achieve a cold-start in the following day.

2.2. PM Characterization. A schematic of the sampling system adopted for this study is shown in Figure 1. Two filter holders hosting quartz (47 mm Pallflex TISSU Quartz 2500 QAT-UP) and polytetrafluoroethylene (Teflon−47 mm Pallflex TX40HI20-WW) filters (herein referred to as Q1 and T1 filters, respectively) were used to collect PM samples of the diluted exhaust directly from the CVS tunnel. In addition, a versatile aerosol concentration enrichment system (VACES) was employed to concentrate the aerosol from the CVS from 106.5 to 6.0 L/min. The VACES (*19, 20*) was operated in line with an impinger (BioSampler, SKC WEST INC., Fullerton, CA) where milligram amounts of particles were collected in Milli-Q water for later use in toxicological assays. Four out of the 6.0 L/min of aerosols in the VACES were drawn through the biosampler, whereas 2.0 L/min were drawn through two additional filters, installed in parallel with the biosampler branch, namely Q2 (Quartz) and T2 (Teflon). The T2 and Q2 filters were preceded by a diffusion dryer, similar to configurations used in our previous studies (*12*). These filters collected the same aerosol supplied to the biosampler. The nominal flow rates through Q1, Q2, T1, and T2 filters and the biosampler were recorded by TSI 4043 flow meters with a certified accuracy of 2% of the reading.

After sampling, Q1, Q2, T1, and T2 filters were conditioned in a constant humidity (40%) and temperature (22 °C) chamber for 24 h to equilibrate the mass of the collected PM. T1 and T2 filters were weighed before and after sampling using a Mettler-Toledo MX5 microbalance (Mettler-Toledo, Columbus, OH; weight uncertainty ±1 μg) to determine the

TABLE 1. Mass and Chemical Species Emissions (mg/km) for Each Vehicle/Configuration

	PM mass (mg/km)	OC (mg/km)	EC (mg/km)	WSOC (mg/km)	nitrate (mg/km)	sulfate (mg/km)	ammonium (mg/km)	sum of inorganic ions (mg/km)
Accord diesel	27.1	4.92	19.6	0.91	0.38	0.07	0.02	1.00
DPF-Accord diesel	0.63	0.51	0.03	0.10	0.08	0.10	0.02	0.31
Corolla gasoline	2.41	0.95	0.05	0.34	0.01	0.99	0.29	1.46
Golf diesel	72.1	24.2	39.1	1.48	0.14	0.14	0.02	0.64
Golf biodiesel	41.2	24.4	6.73	1.42	1.18	0.26	0.01	2.79

mass of the collected PM. Laboratory filter blanks were also weighed before, during, and after each weighing session to verify the accuracy and consistency of the microbalance. The chemical data presented in this paper refer to the Q1 and T1 filters only, whereas the Q2 and T2 substrates were archived for further toxicity and organic speciation analyses, which are currently underway.

Five T1 and five Q1 filter samples (one per cycle) were collected for each high emitting vehicle (all diesel configurations without DPF), whereas one Quartz and one Teflon composite filter sample was collected for all cycles in the low-emitting vehicle cases (gasoline and diesel with DPF). The low-emitting vehicles were tested twice to increase confidence due to their low emission levels.

2.3. Chemical Analysis. All Teflon substrates were separated into two sections for chemical analysis. Half of the filter was analyzed for WSOC using a Sievers Total Organic Carbon analyzer (General Electric Inc.) (*21*). The remaining half was used to determine the concentration of several ionic species (i.e., chloride, nitrate, phosphate, sulfate, sodium, ammonium, and potassium) by ion chromatography (IC). Lough et al. (*22*) described the procedures followed for sample processing in the IC and ICP-MS analyses. The quartz substrates were used for elemental carbon (EC) and organic carbon (OC) analyses, conducted according to the NIOSH Thermal Desorption/Optical Transmission method (*23*).

A chemical assay based on the consumption of dithiothreitol (DTT) in a cell-free system was conducted on liquid suspensions collected with the biosampler to evaluate the toxic activity of these samples. This assay provides a measure of the overall oxidative potential of a PM sample based on its ability to catalyze electron transfer between DTT and oxygen in a simple chemical system (*24*). It is sensitive to the oxidative activity of organic compounds in the PM suspension used for the assay, and it is particularly appropriate for motor vehicle exhaust. The electron transfer is monitored by the rate at which DTT is consumed under a standardized set of conditions, and this rate is proportional to the concentration of the catalytically active redox-active species in the sample (see ref *24* for further details). All PM samples were shipped from the field to the laboratory on dry ice and stored frozen at −20 °C until assayed.

3. Results and Discussion

3.1. PM Mass Emissions. Table 1 shows the mass emission rates (mg/km) of PM and selected chemical species (OC, EC, WSOC, nitrate, sulfate, ammonium, and sum of inorganic ions) from the analyses of the Q1 and T1 filters ("upstream" of the VACES). Values for each vehicle are composited over all driving cycles. The upstream reconstructed mass [i.e., sum of EC, OM (organic material), and inorganic ions] expressed in mg/km driven as a function of the gravimetrically determined PM mass concentration (T1) is shown Figure S1 (see the Supporting Information). To account for the mass of the noncarbonaceous organic components measured, OC has been multiplied by a factor of 1.43, 1.55, and 1.34 for the Accord, the Corolla, and the Golf vehicles, respectively (*25*). The factors were calculated on the basis of the relative water soluble organic carbon (WSOC) vs water insoluble organic carbon (WISOC) contributions to OC in each vehicle.

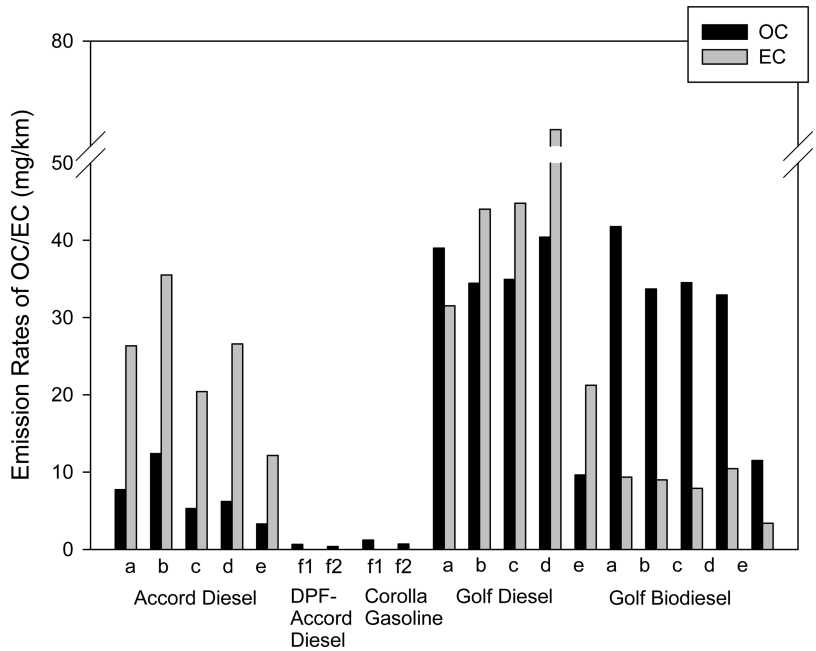

FIGURE 2. Emission rates (mg/km) of organic carbon (OC) and elemental carbon (EC) for each vehicle/configuration: (a) NEDC cycle, (b) Artemis urban cycle, (c) Artemis road cycle, (d) Artemis motorway cycle, (e) 90 km/h steady state, (f1) all cycles composite on the first day, and (f2) all cycles composite on the second day.

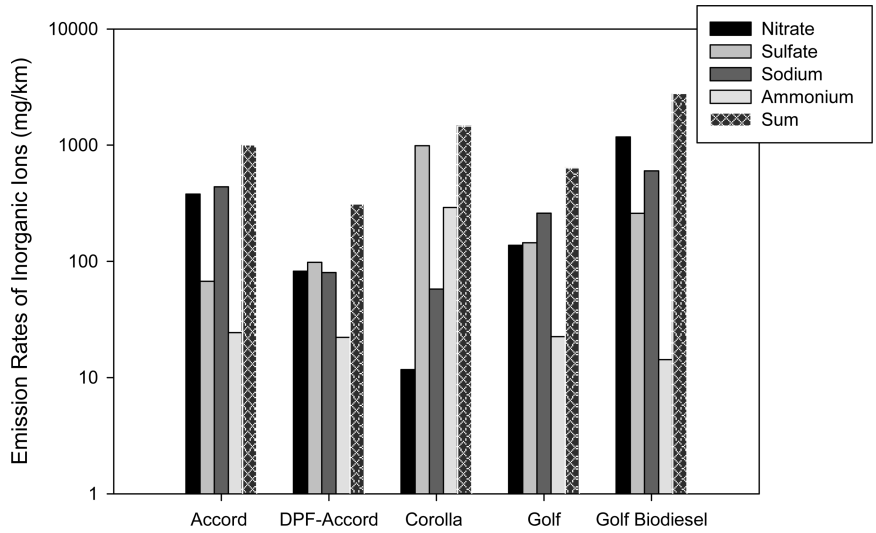

FIGURE 3. Emission rates of selected inorganic ions (mg/km) for each vehicle/configuration.

Measured and reconstructed PM mass were highly correlated (slope = 0.99, $R^2 = 0.99$) and on average agreed within 10% or less.

The baseline Golf diesel vehicle, which corresponds to the older emission control technology, was characterized by the highest emission rates, followed by the Golf biodiesel with oxidation catalyst and the Accord diesel passenger vehicles. Both the DPF-diesel and gasoline vehicles emitted substantially lower PM. Actually, PM mass emissions from the DPF-diesel vehicle were even lower than those from the gasoline vehicle, thus highlighting the effectiveness of the DPF.

3.2. Chemical Composition. The percentage contribution of different chemical species to total emission rates from each vehicle is shown in Figure S2 (see the Supporting Information). A factor of 2 was used to convert WSOC to water soluble organic matter (WSOM), while WISOC was multiplied by 1.3 to obtain water insoluble organic matter (WISOM) (*25*). EC represented the highest PM fraction in the Accord and baseline Golf emissions, at 73% and 55%, respectively, and decreased significantly in the biodiesel Golf (15% of PM). This demonstrates the strong impact of the oxygen atoms in the biodiesel ester on soot formation and oxidation. The contribution of EC on total PM emissions further decreased in the DPF-diesel, which underscores the effectiveness of the DPF system in filtering soot emissions. Further, to EC, all species measured varied considerably between the five configurations. Inorganic ions, ammonium, and sulfate, in particular, were the highest contributors to the PM emitted from the gasoline vehicle tested (>50%) but were less than 1% in the case of the baseline diesel car without exhaust aftertreatment.

3.3. Emission Factors of Organic Carbon (OC) and Elemental Carbon (EC). Depending on the vehicle and emission control, three configurations (Accord diesel, Golf diesel, and Golf biodiesel) allowed collection of sufficient PM mass on the "upstream" filters for a detailed analysis of each driving cycle. The DPF-equipped Accord diesel and Corolla gasoline cars were analyzed as composited samples over all driving cycles. Figure 2 illustrates the OC and EC emission data (mg/km) for each driving cycle of the higher emitters and as composite samples for the lower emitters. For the three high emitters, steady state emissions were 27−62% and 29−67% lower than those from other driving cycles for OC and EC, respectively. With the exception of the DPF-diesel vehicle, all diesel cars were characterized by higher emission rates for OC and EC compared to the gasoline vehicle. When the DPF was employed, OC and EC emissions were decreased by 90 and 99%, respectively. Although the DPF mostly captures soot particles, which are collected in the monolith by filtration, the significant reduction in tailpipe EC lowers the PM surface area available for condensation of semivolatile organic vapors, which may lead to a decrease in OC concentrations in the exhaust. In addition, the oxidative activity of the particular DPF offers a second mechanism for OC reduction.

TABLE 2. DTT Consumption Rates [Expressed in nmol/(min × μg) and nmol/(min × km)] for Each Vehicle/Configuration

	DTT consumption rate	
	nmol/(min × μg) ± SD	nmol/(min × km) ± SD
Accord diesel	0.023 ± 0.002	624 ± 54.3
DPF-Accord diesel	0.019 ± 0.002	12.0 ± 1.3
Corolla gasoline	0.012 ± 0.001	29.1 ± 2.4
Golf diesel	0.018 ± 0.003	1300 ± 216
Golf biodiesel	0.025 ± 0.003	1040 ± 124

The use of biodiesel decreased EC emissions and the relative contribution of EC to measured total carbon (TC = OC + EC) by 70 to 85% across the different driving cycles. Oxygen in the biodiesel ester atoms inhibits in-cylinder soot production by both disrupting the carbon chain development and promoting oxidation. Interestingly, the OC emissions for the baseline and biodiesel Golf configurations were very similar across all driving cycles, despite the use of an oxidation catalyst in the latter. In general, biodiesel should lead to an increase in OC, as a result of its chemical composition and the higher viscosity and density, all of which degrade the spray and combustion quality (*16*). However, the combined use of biodiesel and catalyst lead to comparable levels of total OC emissions, as the effect of biodiesel seems to be counterbalanced by the oxidation activity of the catalyst.

As shown in Table 1, the Accord diesel, Golf diesel, and Golf biodiesel cars emitted similar levels of WSOC (0.91−1.48 mg/km). EC, WSOC, and WISOC emissions were significantly lower in the DPF-diesel and the gasoline vehicles (0.03−0.05 mg/km, 0.1−0.34 mg/km, and 0.41−0.61 mg/km, respectively). An earlier study by Biswas et al. (*26*) indicated lower WSOC/OC ratios (hence, a lower solubility) in PM emissions of baseline diesel heavy-duty vehicles compared to retrofitted ones. This is consistent with the low WSOC/OC ratio observed in this study for the baseline Golf diesel vehicle (∼0.06). The newer Accord diesel and DPF equipped Accord diesel cars showed higher OC solubility (WSOC/OC of ∼0.19).

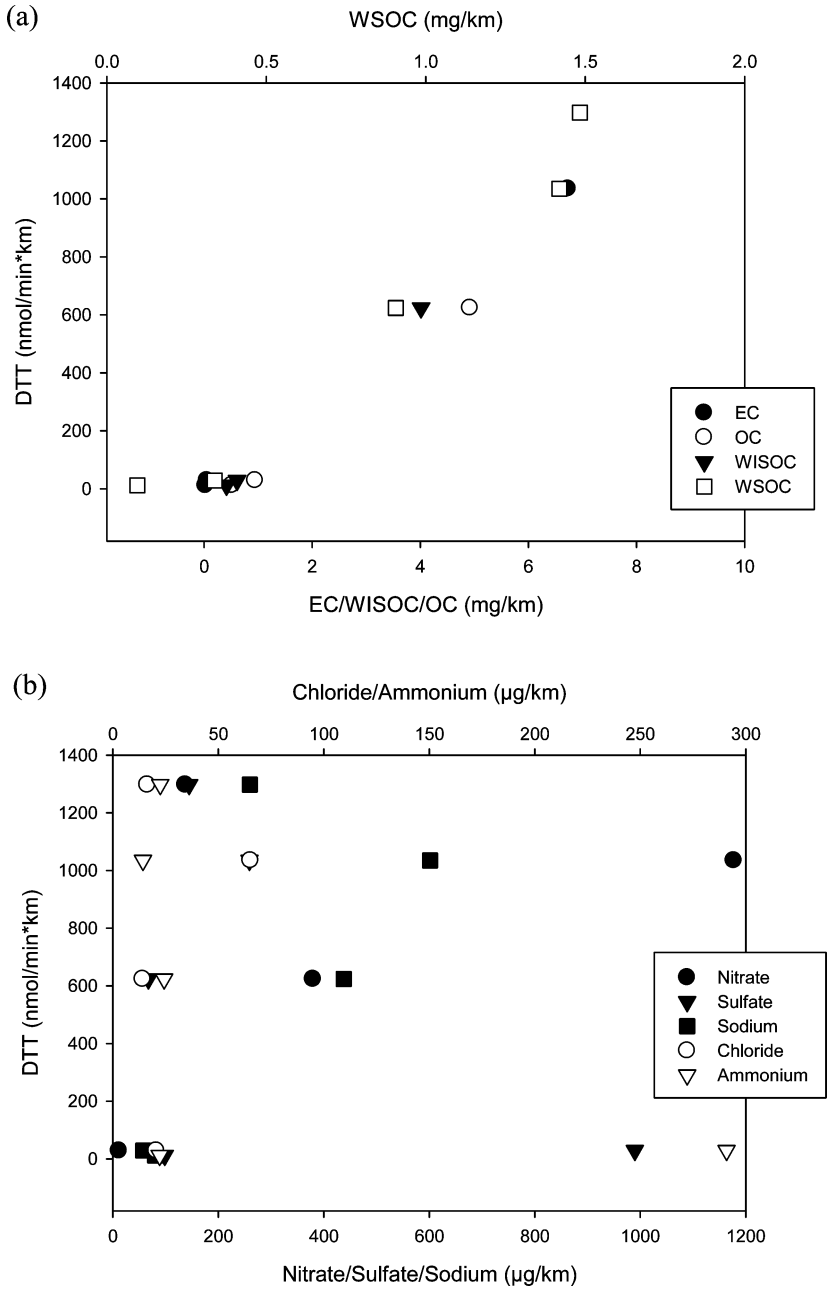

FIGURE 4. Correlation plots between chemical species and the corresponding DTT consumption rates of particulate matter from each vehicle configuration: (a) elemental carbon (EC), organic carbon (OC), water insoluble organic carbon (WISOC) and water soluble organic carbon (WSOC), (b) nitrate, sulfate, sodium, chloride, and ammonium.

3.4. Emission Factors of Inorganic Ions. Figure 3 shows the emission rates (mg/km) for the analyzed inorganic ionic species. The biodiesel car with the oxidation catalyst was the overall highest emitter of inorganic species, followed by the gasoline car, despite the very low mass emission levels of the latter. Sulfate emission was highest for the gasoline vehicle due to the very low sulfur level (less than 10 ppm) of the diesel cars with oxidation aftertreatment. Interestingly, the biodiesel vehicle is a higher sulfate emitter than the petrodiesel Golf, despite the zero sulfur level in the biodiesel fuel. Sulfate in the biodiesel car likely originates from lube oil sulfur, which is converted to sulfate by the oxidation catalyst.

Ammonium emissions from the gasoline vehicle were 12−20 times higher than the diesel vehicles. This is likely the effect of increased formation of ammonia induced by the three-way catalytic converter of this vehicle, consistent with observations of other studies (*27*, *28*). Kean et al. (*28*) showed that increased ammonia emissions are an inadvertent effect of three-way catalytic converters in light duty gasoline vehicles, whereas heavy-duty diesel trucks are a minor source of ammonia emissions by comparison.

The opposite trends of NO_3^-/NH_4^+ between the Golf and Golf biodiesel cars are also of interest. The highest nitrate emission in the latter is expected due to the general increase in NO_x emissions using biodiesel (*16*) and the oxidation activities of the catalyst. The subsequent oxidation of ammonia by nitrogen dioxide over the catalyst may be responsible for the lower ammonium ion emission rate in the biodiesel car. The effects of different aftertreatment devices on inorganic ion formation may be an important consideration, as recent studies suggest that combustion-generated ions may play a critical role in the formation of semivolatile nanoparticles by heterogeneous nucleation (*26*, *29*).

3.5. Oxidative Potential from Different Vehicles and Configurations. Table 2 shows the DTT consumption rates

TABLE 3. Pearson Correlation Coefficients (*R*), Corresponding Significance Levels (*P*), Regression Slopes (*m*) [nmol/(min × mg)] or [nmol/(min × μg)], and *y*-Intercepts [nmol/(min × km)] between DTT Consumption Rates [nmol/(min × km)] and Various Chemical Species [(mg/km) or (μg/km)]

species	EC	WSOC	WISOC	OC	chloride	nitrate	phosphate	sulfate	sodium	ammonium
Pearson *R*	0.80	0.98	0.93	0.94	0.28	0.51	0.16	−0.45	0.69	−0.56
P-value	0.11	<0.01	0.02	0.02	0.72	0.38	0.84	0.44	0.20	0.33
regression slope	27.9	915	46.4	44.5	6.43	0.61	4.20	−0.68	1.72	−2.68
y-intercept	234	−177	128	1310	560	380	656	813	106	800

both on a per PM mass [nmol/(min × μg)] and a per km driven [nmol/(min × km)] basis for each vehicle/configuration. On a per PM mass basis, the Accord without DPF and the Golf running on biodiesel produced the most potent exhausts but, while the per km oxidative activity of the latter vehicle is one of the highest measured [1040 ± 124 nmol/(min × km)], that for the Accord diesel car is substantially lower [624 ± 54.3 nmol/(min × km)] because of the relatively lower mass emissions.

Not surprisingly, the DTT consumption rate of the Golf diesel car (expressed on a per km driven basis) was the highest among all studied vehicles/configurations [1300 ± 216 nmol/(min × km)], because it emitted the highest amount of PM mass and other oxidative-active species such as OC, EC, and WSOC. Interestingly, although the use of biodiesel and a catalyst reduced PM mass emissions by 43% (from 72.1 to 41.2 mg/km), the corresponding decrease in oxidative potential was only 20% [from 1300 ± 216 nmol/(min × km) to 1040 ± 124 nmol/(min × km)], probably because both the Golf diesel and the Golf biodiesel vehicles released similar amounts of OC (24.2 and 24.4 mg/km, respectively). The DPF-equipped Accord diesel car was characterized by the lowest per km oxidative activity [12.0 ± 1.3 nmol/(min × km)], which suggests that, overall, DPF technology is effective in reducing the actual toxicological impact of diesel emission on human exposure. The oxidative potential of the DPF diesel vehicle was roughly 60% lower than that of the only gasoline vehicle tested (also characterized by a very low oxidative activity), because of its comparatively lower mass emissions.

3.6. Correlations between Chemical Constituents and DTT Consumption. Correlations between DTT consumption rates [nmol/(min × km)] and chemical constituents (mg/km) were used to assess the toxicological contribution of each chemical species. Since the speciation data were obtained from the analysis of filters collected "upstream" of the VACES, but the DTT analyses were conducted on concentrated liquid suspensions from the biosampler ("downstream" of the VACES), the relationships between "upstream" and "downstream" emissions rates were investigated. The comparison between the PM masses reconstructed as the sum of EC, OM, and inorganic ion measurements from filters collected "upstream" and "downstream" of the VACES is shown in Figure S3 (see the Supporting Information). The theoretical concentration enrichment factor (*16*) was used for the T2 calculations because particles were collected downstream of the VACES. "Upstream" and "downstream" emissions were in good agreement ($R^2 = 0.79$) with a slope of 1.13 between the "upstream" and "downstream" PM mass rates.

Figure 4a,b shows the correlation plots between DTT consumptions rates and various PM chemical species. Carbonaceous species (EC, WSOC, WISOC, OC) show good correlations with DTT consumption rates. In contrast, there is no correlation between the oxidative potential of the exhaust and the emission rates of inorganic ions (chloride, nitrate, sulfate, sodium, and ammonium), consistent with previous studies by our group (*30*). Pearson correlation coefficients (*R*), corresponding significance levels (*P*), regression slopes, and *y*-intercepts are shown in Table 3. The DTT consumption rate based on the distance driven was best correlated with WSOC ($R = 0.98$, $P < 0.01$), which is also consistent with earlier studies (*15, 31*). The strong positive impact of WSOC on DTT consumption rates is also evidenced by the high regression slope (915 nmol/min/mg), much higher than any other species.

In summary, our results have shown lower emissions and distance-based oxidative potential for the DPF-diesel and gasoline cars, while diesel and biodiesel vehicles released the highest amount of most PM species and the most potent exhaust in terms of oxidative potential. A correlation analysis showed that distance-based oxidative activity is strongly associated with the WSOC content of the exhaust, and to a lesser degree, with OC and WISOC.

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Supporting Information Available

Table of general information of each vehicle and figure of the correlation between reconstructed mass emissions and gravimetrically determined PM mass emissions, of the percentage contributions of EC, WSOM, WISOM, and inorganic ions to the total emission rate from each vehicle tested, and of the comparison between PM masses reconstructed as the sum of EC, OM, and inorganic ion measurements from filters collected "upstream" and "downstream" of the VACES. This material is available free of charge via the Internet at http://pubs.acs.org.

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